

polar media involve a monomeric form analogous to that in salt **2**, where the "half-naked" side of the metal ion is ligated by a water molecule or molecules, and (ii) water dissociates from the complex in nonpolar membranes to give rise to the "half-naked" monomer or polymer similar to that in salt **1**, with an appropriate degree of polymerization.⁴⁰

Conclusion

Thallium salt **1** contains doubly rare structural aspects, a polymeric structure and metal-phenyl π -bonding, but still obeys a structural principle for ionophore-metal complexes, that is, three-dimensional nonpolar protection of the metal ion. On the other hand, the structure of thallium salt **2** is quite unexpected, the monomeric structure with the metal ion being "half-naked", and thus provides, to our knowledge, the first example that deviates from this rule. Furthermore, the "half-naked" side of the molecule is surrounded by nonpolar groups in the crystal structure, suggesting that the "less-screened" structural form also exists in the lipid membranes, at least for the lasalocid A-thallium(I) system.

(40) At the present stage, we cannot exclude a dimer form in nonpolar environments, since there is a preference of dimers over monomers for lasalocid A-metal structures; a model-building consideration supports this (Figure S1¹³). Thus we have now concentrated our efforts on producing a dimer salt in nonpolar solvents.

Clearly, further X-ray studies of metal salts involving different circumstances, possibly crystallization from solvents of different polarities, are necessary to understand the entire mechanism of metal ion capture and release by lasalocid A.^{1a}

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Supplementary Material Available: Tables of anisotropic temperature factors (Tables S1 and S2), atomic coordinates for hydrogen atoms (Tables S3 and S4), ¹³CNMR and ¹H NMR spectral data for **2** (Table S7), least-squares planes (Table S8), model-building calculations of the nearest-neighbor contacts around the assumed water ligand for **2** (Table S9), torsion angles (Table S10), metal binding sites and distances in various lasalocid A-metal salts (Table S11), model-building estimations of the rotation effects of the carboxyl group of the lasalocid A on the intramolecular hydrogen-bonding formation (Table S12), and polymorphism in the various lasalocid A crystal structures (Table S13) and the structural model for a [Tl⁺(lasalocid A⁻)₂] dimer (Figure S1) (17 pages); listings of observed and calculated structure factors (Tables S5 and S6) (12 pages). Ordering information is given on any current masthead page.

Polar/ π Interactions between Stacked Aryls in 1,8-Diarylnaphthalenes

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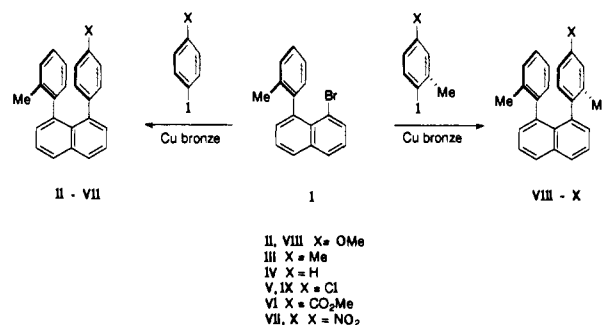
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Abstract: A series of substituted 1,8-diarylnaphthalenes, II-X, has been prepared, and the barrier to rotation about the aryl-naphthalene bond has been measured. A monotonic increasing relationship between ΔG^\ddagger and σ_{para} values has been found. This is interpreted in terms of a through-space polar interaction between the two aryl units.

The energy for the interaction of two arene units divides roughly into a Coulombic (polar) and a van der Waals (dispersive) term.^{2,3} The vdW term depends strongly on the contact surface area whereas the Coulombic term depends on the relative charge distribution. In the case of two benzenes, the surface area, and hence the vdW term, is relatively small; therefore, the Coulombic term dominates the interaction.⁴

A simple picture of the electron distribution in benzene shows an electron-rich central core surrounded by an electron-poor toroidal periphery.⁵ Thus, the Coulombic term is repulsive in the parallel-stacked geometry.^{3,6} This accounts well for the preference

Scheme I



of the herringbone structure of crystalline,⁷ liquid,⁸ and gaseous⁹ benzene.¹⁰

(6) An alternate description, presented by Sanders,^{2a} depicts the charge distribution as a sandwich with negative regions at top and bottom and a positive region in between.

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 (2) Sanders^{2a} cites the four-term equation, $E_{\text{total}} = E_{\text{electrostatic}} + E_{\text{induction}} + E_{\text{dispersion}} + E_{\text{repulsion}}$,^{3b} to partition the energy of a molecular interaction. Jorgensen^{3c} prefers a "Coulomb plus Lennard-Jones format".

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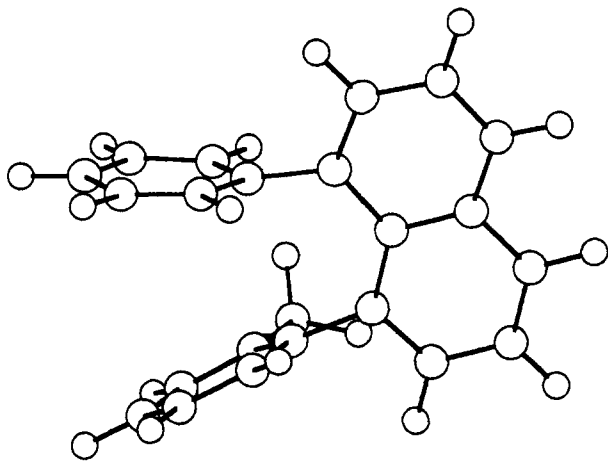


Figure 1. Structure of IV as determined by semiempirical methods using the AM1 Hamiltonian.

Table I. Barriers to Rotation for Naphthalenes II–VII

compd	substituent	ΔG^\ddagger
II	OMe	13.9
III	Me	14.4
IV	H	14.7
V	Cl	15.5
VI	CO ₂ Me	16.9
VII	NO ₂	17.3

Steric effects, such as those found in 1,8-diphenylnaphthalenes, force the phenyl groups into a stacked geometry.^{11,12} During the rotation of a phenyl group by 180° the parallel-stacked interaction is lost; thus, all else being equal, the barrier to rotation should vary with the strength of the parallel-stacked interaction. Based on this simple analysis, we began a study of the barrier to rotation in a series of 1-(4-X-phenyl)-8-(2-methylphenyl)naphthalenes and 1-(4-X-2-methylphenyl)-8-(2-methylphenyl)naphthalenes. We report herein a general trend in these rotational barriers consistent with a polar interaction between the two arenes.

Results

We synthesized two series of 1,8-diarylnaphthalenes (Scheme I) starting from the coupling of 1,8-dibromonaphthalene with 2-methyliodobenzene under Ullmann conditions to give 1-bromo-8-(2-methylphenyl)naphthalene (I). The first series (II–VII) was prepared by coupling of I with the respective 4-X-iodobenzene, again under Ullmann conditions. The second series (VIII–X) was similarly produced from I and the appropriate 2-methyl-4-X-iodobenzene.

The X-ray structure of 1-(2-methylphenyl)naphthalene¹² shows that the best plane of the phenyl ring is perpendicular to that of the naphthalene. Semiempirical calculations using AM1 Hamiltonian¹³ predict the structure of II–X to have the aryl rings perpendicular to the naphthalene plane (Figure 1). This dis-

Table II. Barrier to Rotation for Naphthalenes VIII–X

compd	substituent	ΔG^\ddagger (kin. epim)	ΔG^\ddagger (2-D NMR)
VIII	OMe	23.8	24.8
a	H	24.1	–
IX	Cl	24.2	25.7
X	NO ₂	24.8	26.1

^aSee ref 11.

position of the methyl of the 2-methylphenyl group renders the two sides of the naphthalene diastereotopic and provides the appropriate symmetry environment to study either series of compounds by NMR techniques.

Room temperature 300-MHz ¹H NMR spectra of all compounds in series 1 (II–VII) showed distinct signals for the o/o' and m/m' hydrogens respectively, consistent with the perpendicular geometry described above and restricted rotation of the phenyl group. Warming of the samples in dimethyl sulfoxide was accompanied by a coalescence of the o/o' and m/m' signals. From line shape analysis, the barrier to rotation for the phenyl group of each compound was determined. The barrier was lowest for X = OMe (II), $\Delta G^\ddagger = 13.9$ kcal/mol, and increased monotonically across the series to X = NO₂ (VII), $\Delta G^\ddagger = 17.3$ kcal/mol (see Table I).

The perpendicular geometry in series 2 (VIII–X) resulted in a mixture of two diastereomers, syn and anti, as was observed by Roberts¹¹ for the compound with X = H. The anti:syn ratio in all mixtures was roughly 3.5:1 (¹H NMR); the same value was found by Roberts.¹¹ For this series of compounds, the barrier to rotation was too high to be obtained by normal line shape techniques. The three compounds with X = OMe, Cl, and NO₂ (VIII–X) were enriched in the anti diastereomer. The barrier to isomerization was determined by following the kinetic epimerization in chloroform. Again, the barrier was lowest for X = OMe and highest for X = NO₂.

Although the barrier in these compounds was unattainable by direct line shape analysis, we were able to use a recently described method for obtaining quantitative rate data from 2D-NOESY spectra.¹⁴ Application of this method at 145 °C in dimethyl sulfoxide-*d*₆ yielded barriers for the compounds in series 2.

The barriers found by 2D-NOESY methods are in agreement with those found by kinetic epimerization. The difference in the barriers obtained by the two methods comes from the difference in temperature at which the determination was made, 40 °C for the kinetic epimerization and 145 °C for the 2-D NMR study. Assuming a ΔS^\ddagger term of ca. –5 eu brings the quantitative values in accordance with one another (Table II).

Discussion

A priori there are at least four different scenarios for the variance in the barrier to rotation across the series of compounds we have studied: (1) no interaction; (2) conjugation of the phenyl groups with the naphthalene spacer; (3) charge transfer between the two phenyl groups; (4) through-space Coulombic interaction between the two phenyl groups.

(1) **No Interaction.** This case is the trivial one and should show no change in either ground-state or transition-state energy as a function of ring substitution. The resulting plot of ΔG^\ddagger vs " σ " would be a line with slope equal to 0.

(2) **Conjugation of the Rotating Phenyl Group with the Naphthalene Spacer.** This should exert the strongest effect on the transition state to rotation of the phenyl group, i.e., when the aryl/naphthalene torsion angle is closest to 0°. Both methoxy- and nitro-substituted arenes should be able to conjugate better than an unsubstituted ring. The compound containing hydrogen in the para position should yield a higher barrier than those containing methoxy or nitro.

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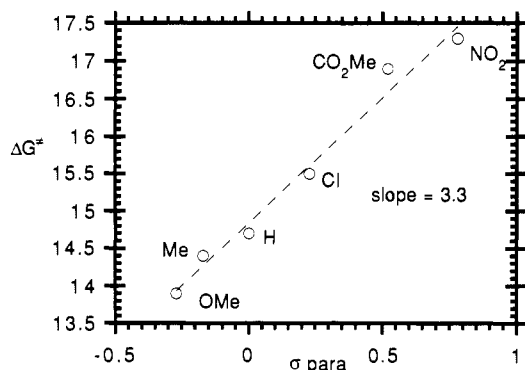


Figure 2. Plot of barrier to rotation (ΔG^\ddagger) vs σ_{para} for naphthalenes II-VII. The slope corresponds to $-2.303RT\rho$.

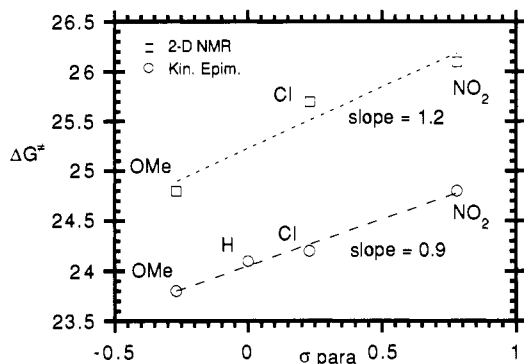


Figure 3. Plot of barrier to rotation (ΔG^\ddagger) vs σ_{para} for naphthalenes VIII-X. The slope corresponds to $-2.303RT\rho$.

(3) **Charge-Transfer Interaction between the Two Phenyl Groups.** Here the stabilization should be most strongly felt in the ground state. Both the methoxy- and nitro-substituted arenes should interact with the neutral arene. The expected plot of ΔG^\ddagger vs σ_{para} would have the compound bearing hydrogen in the para position lower than those bearing methoxy or nitro. In addition, one would expect to see a charge-transfer band in the UV spectra of these compounds.

(4) **Through-Space Coulombic Interaction between the Two Phenyl Groups.** As noted in the introduction, the Coulombic term for two parallel-stacked arenes is repulsive, and the center of unsubstituted benzene is electron rich. Therefore, substitution of hydrogen by an electron-donating group such as methoxy should increase the repulsion and raise the energy of the parallel-stacked conformation. Substitution of hydrogen by an electron-withdrawing group such as nitro, on the other hand, should reduce the repulsion and lower the energy of the parallel-stacked state. This should result in an increase in barrier height with increasing electron-withdrawing character, and a plot of ΔG^\ddagger vs " σ " should increase from methoxy to nitro, with hydrogen in between.

The trend for the barriers in the two series (II-VII, VIII-X) studied is the same (Figures 2 and 3). For X = OMe, an electron-donating group, the barrier is lowest, and for X = NO₂, an electron-withdrawing group, the barrier is highest.

No UV absorptions were seen above 350 nm. The spectrum of I, where there is only one phenyl group, is essentially the same as for II-X. In addition, the spectra of II-X can be accounted for by a simple composite of a naphthalene and a phenyl chromophore. *There is no spectroscopic evidence for a significant charge-transfer interaction between the arenes.*

Conjugation effects on the barrier to rotation in 4,4'-disubstituted biphenyls have been reported, but the magnitude of this effect is small compared to what we see here.¹⁵ The biphenyl series should show a larger conjugation effect than either series

1 or 2. *There is no evidence to say that conjugation plays a significant role in determining this behavior.*

It is possible that a combination of effects might account for the observed trend; however, by Occam's razor we conclude that a through-space Coulombic interaction between the two phenyl groups is the most likely explanation for the variance observed in the barrier to rotation across series 1 and 2.

Trends of this type have been seen elsewhere in the literature.^{16,17} Oki¹⁶ studied the isomerization of a series of 9-(2-hydroxy-1-naphthyl)fluorene benzoates, featuring different para substituents on the benzoate moiety, from *sp* to *ap* and from *ap* to *sp* conformations. In the *sp* → *ap* isomerization where the fluorene and the benzoate overlap in the ground state, he noted an effect on the barrier to interconversion. The barrier for the methoxy-substituted compound was lowest, and that for the nitro was highest. However, the *ap* → *sp* process, where such overlap was not possible, showed no change in barrier with substitution.

This is completely consistent with the polar/ π hypothesis. Only in the *sp* conformer do the arene units interact; substitution varies the energy of the ground state, and thus the *sp* → *ap* barrier. In the *ap* conformer, no interaction is possible and there is no variance in the *ap* → *sp* barrier.

Diederich¹⁷ showed that molecular complexation of a series of disubstituted naphthalenes with an electron-rich host followed a trend in binding from dimethoxy (weakest) to dicyano (strongest). No charge-transfer bands were seen in the spectra, and he concluded that purely polar effects were responsible for the trend.

The polar/ π effect has also been invoked to explain the interaction between ions and arenes, such as carboxylate-arene¹⁸ and trimethylammonium-arene interactions.¹⁹ Indeed, the hydrogen bonding seen between amines and arenes in proteins has been rationalized as a manifestation of the polar/ π nature of arenes.²⁰ Recently, even water has been reported to hydrogen bond to aromatic cyclophanes.²¹ Systems similar to the one presented here, with varying substituents and steric demands, can be used to address the question of sensitivity for these interactions as well.²²

Conclusion

We synthesized two series of substituted 1,8-diarylnaphthalenes and studied the variance of the barrier to aryl-naphthalene bond rotation as a function of aryl substitution. In both cases, the barrier increases monotonically on passing from an electron-donating to an electron-withdrawing substituent. This finding, together with other experimental evidence, led us to conclude that a significant through-space polar/ π interaction exists between the two phenyl units.

Experimental Section

General Data. ¹H and ¹³C NMR were recorded on Varian XL-300 and Varian Unity 500 instruments in CDCl₃. Chemical shifts were referenced downfield from TMS. UV spectra were obtained on a Perkin-Elmer Lambda 6 instrument. Silica gel was used for analytical, gravity, and flash chromatography. Melting and boiling points are uncorrected. Iodobenzene, 2-methyliodobenzene, 4-methyliodobenzene, 4-methoxyiodobenzene, 4-chloroiodobenzene, and 4-nitroiodobenzene were used as supplied. 1,8-Dibromonaphthalene (mp 108–109 °C; lit.²³ mp 108.5–109 °C), 4-methoxy-2-methyliodobenzene (mp 43–45 °C; lit.²⁴ mp 43–45 °C), 4-chloro-2-methyliodobenzene (bp 240 °C; lit.²⁵ bp 240

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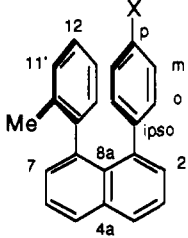
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Table III. ¹H NMR Data for Naphthalenes II–VII


II - VII

H-C	OMe	Me	H	Cl	CO ₂ Me	NO ₂
2	7.25	7.26	7.27	7.26	7.28	7.28
3	7.50	7.51	7.51	7.53	7.52	7.54
4	7.95	7.95	7.96	7.97	7.98	8.02
5	7.92	7.94	7.95	7.96	7.95	7.97
6	7.53	7.53	7.54	7.56	7.56	7.60
7	7.30	7.31	7.30	7.30	7.31	7.32
10	6.96	6.93	6.95	6.93	6.95	6.95
11	6.93	6.90	6.87	6.93	6.88	6.90
11'	6.72	6.67	6.70	6.73	6.78	6.67
12	6.88	6.88	6.85	6.96	6.83	6.88
o	6.71	6.70	6.86	6.72	6.88	6.95
o'	7.03	6.98	7.12	7.03	7.17	7.24
m	6.38	6.63	6.91	6.80	7.55	7.93
m'	6.50	6.75	6.97	6.93	7.67	7.83
Me	1.80	1.81	1.83	1.79	1.82	1.83
X	3.72	2.19	6.97	-	3.91	-

°C), 2-methyl-4-nitroiodobenzene (mp 102–103 °C; lit.²⁶ mp 104 °C), and 4-carbomethoxyiodobenzene (mp 112–113 °C; lit.²⁷ 114 °C) were prepared according to literature procedures.

1-Bromo-8-(2-methylphenyl)naphthalene (I). To a stirred mixture of 1,8-dibromonaphthalene (1.144 g, 4 mmol) and 2-methyliodobenzene (1.02 mL, 8 mmol) heated at 180 °C was added copper bronze (0.6 g) portionwise over a 30-min period. After 4 h of stirring at 180 °C, the reaction mixture was cooled down at room temperature, and acetone (5 mL) was added. After 10 min of stirring, the mixture was filtered, and the precipitate was washed with acetone several times. The filtrate was concentrated in vacuo, and the residue was chromatographed with hexanes as eluant to give compound I in 30–35% yield as a thick oil that solidifies on standing in the refrigerator and melts at room temperature. UV nm (log ε): 230 (4.83); 292 (4.09). Anal. Calcd: C, 68.70; H, 4.41. Found: C, 68.53; H, 4.34.

General Procedure for the Preparation of Compounds II–X. To a stirred mixture of 1-bromo-8-(2-methylphenyl)naphthalene (0.297 g, 1 mmol) and iodobenzene derivative (2 mmol) heated at 180 °C was added copper bronze (0.2 g) portionwise over a period of 30 min, and the mixture was stirred at 180 °C for 12 h. After cooling at room temperature, the reaction was worked up as described for the synthesis of I, and the crude product was purified by flash chromatography with the indicated eluant (NMR data for II–VII is given in Tables III and IV).

1-(4-Methoxyphenyl)-8-(2-methylphenyl)naphthalene (II), mp 119–121 °C, was obtained in 38% yield with hexanes as eluant. UV nm (log ε): 232 (4.70), 290 (4.12). Anal. Calcd: C, 88.85; H, 6.21. Found: C, 88.89; H, 6.14.

1-(4-Methylphenyl)-8-(2-methylphenyl)naphthalene (III), mp 152–154 °C, was obtained in 25% yield with hexanes as eluant. UV nm (log ε): 244 (4.61), 302 (3.97). Anal. Calcd: C, 93.46; H, 6.54. Found: C, 93.27; H, 6.39.

1-Phenyl-8-(2-methylphenyl)naphthalene (IV), mp 131–132 °C, was obtained in 29% yield with hexanes as eluant. UV nm (log ε): 234 (4.68), 292 (4.03). Anal. Calcd: C, 93.84; H, 6.16. Found: C, 93.79; H, 6.11.

1-(4-Chlorophenyl)-8-(2-methylphenyl)naphthalene (V), mp 164–165 °C, was obtained in 32% yield with hexanes as eluant. UV nm (log ε): 243 (4.58), 304 (3.96). Anal. Calcd: C, 84.01; H, 5.21. Found: C, 83.90; H, 5.29.

1-(4-Carbomethoxyphenyl)-8-(2-methylphenyl)naphthalene (VI), mp 132–133 °C, was obtained in 26% yield with a 95:5 hexanes/diethyl ether mixture as eluant. UV nm (log ε) 236 (4.92), 294 (4.44). Anal. Calcd:

Table IV. ¹³C NMR Data for Naphthalenes II–VII

C	OMe	Me	H	Cl	CO ₂ Me	NO ₂
1	140.3	140.7	143.0	140.8	147.5	138.2
2	130.6	130.6	130.6	130.5	130.6	130.9
3	124.9	124.9	124.9	124.9	124.9	124.9
4	128.6	128.6	128.8	129.1	129.4	130.0
4a	135.0	135.0	135.0	135.0	135.0	135.0
5	128.6	128.6	128.5	128.6	128.6	128.8
6	125.1	125.1	125.2	125.3	125.4	125.7
7	130.5	130.5	130.7	130.5	130.6	130.5
8	143.1	143.1	140.8	142.8	142.5	142.5
8a	130.1	130.2	129.9	129.9	129.8	130.0
9	139.8	139.9	139.9	139.5	139.5	139.2
10	130.7	130.8	130.7	130.7	130.8	130.8
10'	135.3	135.3	135.4	135.3	135.3	135.5
11	124.8	124.8	124.8	125.0	125.1	125.3
11'	129.3	129.2	129.3	129.5	129.5	129.6
12	126.4	126.0	126.6	126.6	126.9	127.1
ipso	134.9	139.4	142.6	139.4	147.5	145.8
o	132.1	130.9	130.9	132.1	130.8	131.6
o'	128.8	127.8	127.8	128.9	127.8	128.3
m	111.2	127.7	125.8	126.5	127.8	121.5
m'	111.5	127.4	126.8	126.8	128.2	122.0
p	157.0	135.1	126.6	131.8	127.2	149.5
Me	20.4	20.4	20.4	20.4	20.3	20.3
X	55.3	20.9	-	-	51.9	-

C, 85.20; H, 5.72. Found: C, 85.07; H, 5.64.

1-(4-Nitrophenyl)-8-(2-methylphenyl)naphthalene (VII), mp 189–191 °C, was obtained in 33% yield with a 99:1 hexanes/diethyl ether mixture as eluant. UV nm (log ε): 232 (4.76), 302 (4.17). Anal. Calcd: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.19; H, 4.93; N, 4.04.

1-(4-Methoxy-2-methylphenyl)-8-(2-methylphenyl)naphthalene (VIII), mp 71–72 °C, was obtained in 29% yield with a 99:1 hexanes/diethyl ether mixture as eluant as a 3.5:1 anti/syn mixture of isomers. Anal. Calcd: C, 88.72; H, 6.55. Found: C, 88.88; H, 6.49. ¹H NMR: 7.96–7.20 (m, 6 H, naphthalene protons), 7.06–6.66 (m, 7 H, aryl protons), 3.76 (s, MeO minor isomer), 3.74 (s, MeO major isomer), 1.86, 1.84 (2 s, Me minor isomer), 1.81, 1.79 (2 s, Me major isomer). The isomeric mixture was enriched in the anti isomer by gravity column chromatography with hexanes as eluant on 230–400-mesh silica gel.

1-(4-Chloro-2-methylphenyl)-8-(2-methylphenyl)naphthalene (IX), mp 68–70 °C, was obtained in 25% yield with hexanes as eluant as a 3.3:1 anti/syn mixture of isomers. Anal. Calcd: C, 84.07; H, 5.58. Found: C, 84.20; H, 5.64. ¹H NMR: 7.95–7.13 (m, 6 H naphthalene protons), 7.00–6.66 (m, 7 H aryl protons), 1.85, 1.84 (2 s, Me minor isomer), 1.80, 1.78 (2 s, Me major isomer). The isomeric mixture was enriched in the anti isomer by gravity column chromatography with hexanes as eluant on 230–400-mesh silica gel.

1-(4-Nitro-2-methylphenyl)-8-(2-methylphenyl)naphthalene (X), mp 139–141 °C, was obtained in 35% yield with a 98:2 hexanes/diethyl ether mixture as eluant as a 3.6:1 mixture of anti/syn isomers. Anal. Calcd: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.38; H, 5.35; N, 3.87. ¹H NMR: 7.98–7.10 (m, 6 H naphthalene protons), 7.68–6.66 (m, 7 H aryl protons), 1.96, 1.86 (2 s, Me minor isomer), 1.90, 1.80 (2 s, Me major isomer). The isomeric mixture was enriched in the anti isomer by gravity column chromatography with a 99:1 hexanes/diethyl ether mixture as eluant on 230–400-mesh silica gel.

Kinetic Epimerization. Enriched samples of known isomeric composition of compounds VIII, IX, and X were dissolved in CDCl₃ and placed in thermostated baths at 40 °C. The samples were withdrawn at different intervals of time, immediately cooled at –78 °C in an acetone/dry ice bath, and kept at that temperature until the isomer ratio was determined by ¹H NMR. End points were confirmed by keeping the samples in the thermostated baths overnight and checking the isomer ratios.²⁸

Variable-Temperature NMR Measurements. All variable-temperature experiments were run on the above described 300-MHz NMR instrument. The temperature was regulated by a chilled stream of nitrogen gas. Temperatures were corrected by a calibration graph. A copper-constantan thermocouple was inserted into an NMR tube with solvent at a height similar to that on a normal sample. Thermocouple readings from inside the tube were then correlated to readings from the thermocouple mounted in the probe. This calibration was repeated from time

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(28) Because of the logarithmic relationship between *k* and Δ*G*[‡], the major contribution to the error in determining Δ*G*[‡] is the error in the temperature. On the basis of this assumption we estimate the errors to be at most 0.3 kcal/mol.

to time. Temperatures during a given experimental run were then extrapolated from the calibration curve and the reading from the probe thermocouple. Temperature readings are accurate within 5 °C.²⁸

Exchange rates were determined from the spectral line shape. Line shape analysis was done using the program DNMR-5 available through QCPE.

2-D NMR Exchange Rates. Sample Preparation. NMR samples were prepared by dissolving 3.5–4.1 mg of the diarylnaphthyl derivative in 0.5 mL of DMSO-*d*₆. Each sample contained 0.8 mM Gd(NO₃)₃. The gadolinium nitrate was used as a paramagnetic relaxation reagent to shorten the spin-lattice relaxation times of the methyl protons and decrease the time of the experiment.

NMR Spectroscopy. All spectra were recorded at 500 MHz and 143 °C (ethylene glycol standard).²⁹ Pure absorption two-dimensional exchange (2-D EXSY) spectra were recorded using the pulse sequence delay-90°-*t*₁-90°-*t*_m-90°-*t*₂ and the method of phase cycling described by States et al.³⁰ with alternating block acquisition. The spectra were collected into 1024 data points in each block with quadrature detection using a spectral width of 1500 Hz and a mixing time of 300 ms. Typically, 512 *t*₁ experiments were collected and zero filled to 1 K. For each *t*₁ value, eight scans were signal averaged, with a recycle time of 3 s. A line broadening of 1 Hz was imposed in each dimension prior to Fourier transformation.

Determination of Rate Constants.²⁸ The volumes of the cross peaks and diagonal peaks of the 2-D data sets were evaluated by summing over all data points contained within a chosen peak integration radius. The rate constants for exchange were calculated by solving for **R** in eq 1,

$$I_{ij}(\tau_m) = M_j(0)(e^{-\mathbf{R}\tau_m})_{ij} \quad (1)$$

where I_{ij} is the integrated intensity of the two-dimensional absorption peak at mixing time τ_m , $M_j(0)$ is the equilibrium magnetization of the nuclei in site j , and **R** is a square matrix whose diagonal elements are $R_{jj} = T_{1,i-1} + \sum_i k_{ji}$ and whose off-diagonal elements are $R_{ij} = -k_{ji}$.^{31,32}

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Registry No. I, 141397-24-2; II, 141397-25-3; III, 141397-26-4; IV, 14476-01-8; V, 141397-27-5; VI, 141397-28-6; VII, 141397-29-7; *syn*-VIII, 141435-25-8; *anti*-VIII, 141397-31-1; *syn*-IX, 141397-30-0; *anti*-IX, 141435-23-6; *syn*-X, 141435-24-7; *anti*-X, 141397-32-2; 4-methoxyiodobenzene, 696-62-8; 4-methyliodobenzene, 624-31-7; iodobenzene, 591-50-4; 4-chloriodobenzene, 637-87-6; 4-(methoxycarbonyl)iodobenzene, 619-44-3; 4-nitrobenzene, 636-98-6; 1,8-dibromonaphthalene, 17135-74-9; 2-methyliodobenzene, 615-37-2; 2-methyl-4-methoxyiodobenzene, 63452-69-7; 2-methyl-4-chloriodobenzene, 23399-70-4; 2-methyl-4-nitroiodobenzene, 5326-38-5.

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Infrared Multiple Photon Studies of Alkoxide-Alcohol Complexes

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Abstract: Alkoxide-alcohol complexes, R'OH·RO⁻, were synthesized by an ion-molecule reaction in a Fourier transform ion cyclotron resonance mass spectrometer. Isotope labeling was used to differentiate between the two possible complexes: ROH·R'O⁻ and R'OH·RO⁻. The structure of the complexes was probed using infrared multiple photon dissociation. The ratio of the photoproducts (RO⁻/R'O⁻) was found to depend on the method of synthesis of the complex. This differentiation suggests that the two complexes are distinct; i.e., they retain some memory of their original identity. These results are not consistent with the simple hydrogen-bonded structure, which should have a very low barrier to proton transfer. The possibility of an isomeric structure which does not lie along the minimum energy path for proton transfer is discussed.

Introduction

Simple proton-transfer reactions between alkoxide ions with localized charge are not expected to have large energetic barriers. In solution, the majority of exothermic proton-transfer reactions between nonconjugated ions occur at the diffusion limit.¹ The gas-phase reactivity of alkoxide ions is not expected to differ significantly from that in solution. Indeed, quantum calculations of the gas-phase proton-transfer potential energy surface suggest that it is relatively smooth, with a proton-transfer barrier of less than 1 kcal/mol separating two strongly bound alcohol-alkoxide complexes.^{2,3} This result is substantiated by fractionation factor measurements of methoxide-methanol and ethoxide-ethanol dimers,³⁻⁵ which are consistent with a small proton-transfer barrier.

In another paper, we reported the surprising result that proton-transfer reaction efficiencies of alkoxides with alcohols are slower than expected.^{6a} Thermoneutral proton transfers between

methoxide and methanol, ethoxide and ethanol, and *tert*-butoxide and *tert*-butyl alcohol all displayed reaction efficiencies of ca. 30%,

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